

Immiscible metals.	Solvent metal.	Approximate ratio.
Lead and zinc	Tin	PbZn_6
" "	Silver	Pb_2Zn
Lead and aluminium	Tin	Pb_2Al_7
" "	Silver	Pb_3Al
Bismuth and zinc	Tin	BiZn_{10}
" "	Silver	BiZn_2
Bismuth and aluminium..	Tin	BiAl_{10}
" "	Silver	Bi_2Al

The author has much pleasure in acknowledging the assistance of Mr. Sydney Joyce in carrying out a large proportion of the analytical work requisite for the experiments above described.

VI. "The Conditions of the Formation and Decomposition of Nitrous Acid." By V. H. VELEY, M.A., University Museum, Oxford. Communicated by Professor ODLING, F.R.S. Received April 12, 1892.

Introductory.

Throughout the whole science of chemistry there is possibly no reagent so frequently represented as taking part in various transformations, but of which so little definite is known, as nitrous acid. In many text-books its properties are cursorily discussed in a few lines, while some writers have gone so far as to deny its existence altogether even in the presence of nitric acid. Among the commoner examples of reactions considered to be effected by nitrous acid, it is necessary only to mention the conversion of the primary paraffinoid amines into the corresponding alcohols, the formation of nitroso- and diazo-derivatives, and the preparation of the fulminates. In a previous paper* it was my endeavour to prove that the solution of certain metals in nitric acid was conditioned by the presence of nitrous acid, and the cause of the chemical change explained on the supposition that the acid is alternately formed and decomposed.

As a fitting corollary to these investigations, it seemed worthy of interest to examine to some extent the validity of this hypothesis by endeavouring to imitate the reactions supposed to take place on solution of the metal, either when no metal is present, or when the metallic salt is either present or absent.

The stability of nitrous acid in presence of nitric acid forms also a part of this research, and, conversely, the stability of nitric acid in absence of nitrous acid is discussed.

In the present, as in my former, investigations, it will be under-

* 'Phil. Trans.,' 1891, A, pp. 312—313.

stood that the term nitrous acid is applied to that kind of matter which decolorises potassium permanganate, liberates iodine from potassium iodide, and gives various colour reactions with certain organic bases.

The Formation of Nitrous Acid in Nitric Acid Solution.

Nitrous acid is generally produced directly by the decomposition or reduction of nitric acid effected (i) by heating the acid, (ii) by passing nitric oxide or nitrous fumes into it, (iii) by electrolysis, or more indirectly (iv) by addition of nitrogen peroxide to water, and (v) by decomposition of metallic nitrites with acids. The nature of these several changes, their conditions, and the composition of the solutions obtained form the main subjects of this investigation.

The Methods of Analysis.

The following process was adopted for estimating the respective amounts of nitrous and nitric acids in presence of one another; the total acidity was determined in the usual manner by means of standard alkali, the nitrous acid by means of potassium permanganate; from the factors thus obtained the amount of acidity due to the nitric acid by itself could be readily calculated. It was found by experience not only in the present but also in previous investigations that nitrous acid could not conveniently be estimated by the addition of the permanganate solution until it is no longer decolorised, for the oxidation of the nitrous acid at the end of the operation is gradual and not instantaneous. This point does not seem to have been noticed by the writers on quantitative analysis. Accordingly the method was modified as follows:—The solution of the nitrous acid was added to such a quantity of the standard permanganate, acidified with sulphuric acid, which was judged to be in slight excess over that required to complete the oxidation, and the whole mixture allowed to stand in stoppered bottles for half an hour. The pink liquid was then poured into potassium iodide solution, and the amount of iodine liberated by the excess of the permanganate determined, as customary, by standard sodium thiosulphate solution. There was apparently no risk of any of the nitrous acid escaping oxidation, and thus liberating iodine from the potassium iodide, if the method was carried out as described.

In order to test the accuracy of the process, some purified silver nitrite was recrystallised several times from water, a known quantity of it was weighed out, suspended in water, and decomposed by a slight excess of purified sodium chloride. The amount of nitrous acid calculated as (NO_2) was determined in the solution, and for a test analysis the following may be cited:—

Amount of (NO_2) in 1 c.c. calculated from
the weighed quantity of silver nitrite
taken..... 0.005963 gram.
Amount of (NO_2) in 1 c.c. found 0.005974 „

The process is, therefore, accurate in this particular case to within 1 part in 600. When smaller quantities of nitrous acid were to be estimated, the metaphenylenediamine method was adopted, the coloration produced being compared with a solution containing a known quantity of nitrous acid by means of the form of tintometer described in my former paper (*vide supra*).

The Stability of Nitric Acid.

It seemed worthy of investigation to determine the actual temperature at which traces of nitrogen peroxide begin to be formed in purified nitric acid of different degrees of concentration; hitherto only general statements are given in the text-books.* Samples of acid of sp. gr. 1.5 and 1.4 respectively were purified by the method of blowing a current of air at a temperature of 35° , and thus obtained quite colourless; the latter was diluted (i) with its own volume, and (ii) with three times its volume, of water. An acid of sp. gr. 1.53 was prepared by distillation of recrystallised nitre with sulphuric acid, and the reddish-yellow acid thus obtained was redistilled with an equal bulk of sulphuric acid. A number of attempts were made to render this acid colourless by a current of air or carbonic acid, but, notwithstanding several modifications, these proved unsuccessful. Recourse was, therefore, had to distillation *in vacuo* in an apparatus specially constructed of glass.

The method of operation was as follows:—The slightly yellow acid was placed in the distillation flask, and the receiver kept cooled by a freezing mixture; at a temperature of 45° , and under a pressure of 15 mm., the acid passed over without any visible ebullition. After one-third of the liquid had been condensed, the receiver was changed, and the remainder distilled over; the first portions contained a greater part of the nitrogen peroxide. The second distillate was then redistilled in the same manner, and thus a perfectly colourless liquid was obtained (sp. gr. $0/0 = 1.541$)† containing only 0.011 milli-

* Carius ('Ber. Deut. Chem. Ges.,' 1870, p. 690) states that when pure nitric acid of sp. gr. 1.51 is heated in sealed tubes to a temperature of 150° and upwards, a reddish-yellow liquid is produced, with evolution of oxygen and "nitrous acid gas;" above 250° the liquid contains such an abundance of nitrous acid that it gives a blue colour on addition of a small quantity of water, and on further dilution nitric oxide is evolved. Accordingly, the decomposition of the acid under these conditions is expressible by the equation $2\text{HNO}_3 = \text{N}_2\text{O}_3 + \text{O}_2 + \text{H}_2\text{O}$.

† I am indebted to my colleague Dr. J. Watts for loan of apparatus and assist-

gram of nitrogen peroxide. Attempts to prepare an acid of greater concentration and more free from the peroxide proved unsuccessful.

In the following table are given the amount of nitric acid in 1 c.c. of each of the several samples.

Sample.	Amount of nitric acid in 1 c.c.	Specific gravity 10/10.
I	1.350 grams	1.541
II	1.1890 "	1.512
III	1.0763 "	1.420
IV	0.5183 "	not determined
V	0.2563 "	"

For each experiment 10 c.c. of the acid were placed in a small piece of combustion tubing, which had previously been cleansed by being filled with concentrated nitric acid and allowed to stand for several hours, generally over night. The tubes were then rinsed several times with water, and finally with water redistilled from potassium permanganate. It was hoped that by this method all reducing substances might be completely destroyed. After introduction of the acid the tubes were quickly sealed up and then heated to various temperatures in water or paraffin baths. The experiments were conducted in dull and generally foggy weather, advantageous at least for them, as concentrated nitric acid is decomposed by direct sunlight. At the end of each experiment the 10 c.c. of acid were poured into 100 c.c. of water, and the amount of nitrous acid determined by the metaphenylenediamine method, as explained above; this is then reckoned in terms of nitrogen peroxide, the substance which imparts the yellow tint to the impure acid.

Sample of acid.	Temperature.	Time.	Nitrogen peroxide produced expressed as 0.001 milligram in 1 c.c.
I	30°	90'	0.25
III	"	"	2.9
IV	"	"	0.51
V	"	"	nil

ance in this method of procedure, which both in his and my hands has proved more successful than the air (or carbonic acid) current method, usually described in the text books, when acids of specific gravity greater than 1.5 are required perfectly colourless.

The distillation method, however, presents one of two alternate difficulties: on the one hand, in each repetition of the distillation the proportion of nitrogen peroxide is decreased, on the other, that of the water is increased.

These results show that whereas the amount of nitrogen peroxide present in the most concentrated acid is doubled by heating under the conditions described above, yet the amounts of this same impurity produced in the less concentrated acids are quite inappreciable. A series of other determinations were made at high temperatures, the results of which are given below.

Sample of acid.	Temperature.	Time.	Nitrogen peroxide present. 0·001 milligram in 1 c.c.
I	58°	90'	0·27
III	"	"	2·7
IV	"	"	2·9
V	"	"	not measurable

Sample of acid.	Temperature.	Time.	Nitrogen peroxide present.
I	100°	90'	0·431
III	"	"	0·05
IV	"	"	nil
V	"	"	nil

Sample of acid.	Temperature.	Time.	Nitrogen peroxide present.
II	120°	90'	0·96
III	"	"	0·2
IV	"	"	0·2
V	"	"	nil

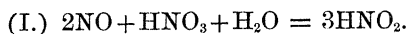
Sample of acid.	Temperature.	Time.	Nitrogen peroxide present.
III	155°	90'	0·70
IV	"	"	0·06
V	"	"	0·06

Sample of acid.	Temperature.	Time.	Nitrogen peroxide present.
III	195°	5'	219
IV	"	"	80

It is manifest from the figures given in the tables above that sample No. I was decomposed to some extent at 58° , and to a greater degree at 100° , sample No. II at 120° , sample No. III at 155° , and very rapidly at 195° , sample No. IV at 195° , while the most dilute acid remained practically unaltered throughout. It would also appear that, provided every care be taken to eliminate reducing substances, especially of an organic character, and provided also that the acids are not unduly exposed to sunlight, nitric acid is more stable than former experience indicated. It would be an interesting subject of enquiry to ascertain as to whether nitric acid is affected by shocks, as I have found that samples of acid purified so as to be practically free from nitrous acid were contaminated with that impurity after a railway journey.

Formation of Nitrous Acid from Nitric Oxide and Nitric Acid.

It is a common matter of observation that when nitric oxide gas is passed into nitric acid a greenish-blue solution is produced, which shows all the reactions of nitrous acid; some writers, however, consider that the nitric oxide gas is only dissolved as such in the nitric acid in that, when the liquid is warmed, the gas is again evolved. It is more probable that nitrous acid is formed and subsequently decomposed, changes represented by the following equations:—



Clemente Montemartini* has proved that of these changes the latter proceed quantitatively, at least in dilute solution, in accordance with the equation given.

If these changes are strictly reversible, it would follow as a necessary consequence that there would be a limit to the amount of the nitrous acid produced, and this limit would be dependent upon conditions such as concentration of acid and temperature. The equation for equilibrium will be

$$p/q = \text{constant},$$

wherein p is the mass of nitric acid, and q is the mass of nitrous acid, for when the limit is reached the amounts of nitric oxide gas passing in and out would be identical, while the alteration of the mass of water would be immaterial.

On the other hand, if the phenomenon is merely that of solution, the amount of nitric oxide gas dissolved should, other conditions remaining the same, diminish under all circumstances as the temperature increases.

* 'Rome, Accad. Lincei Rendiconti,' 1890, p. 264.

To decide between these views, and to determine the limit, whether of nitrous acid formed or of nitric oxide dissolved, as the case might be, a series of experiments were conducted in the following manner.

Nitric acid was passed through an apparatus consisting of (1) a wash-bottle containing soda; (2) a set of Liebig's bulbs; and (3) a set of Geissler's bulbs both filled with nitric acid of the same concentration, the latter of which was used for the analytical determinations; and (4) a wash-bottle containing soda to prevent any nitrous fumes, produced by the passage of the unaltered nitric oxide into the air, from accidentally coming in contact with the acid experimented upon. In these and succeeding experiments the apparatus consisted wholly of glass, except for small pieces of rubber tubing which served for connections; these were frequently renewed. Before the nitric oxide was passed, the whole apparatus was filled with hydrogen, my previous experiments having shown that this gas, when ready-made, does not reduce nitric acid, but even mechanically blows off any slight impurity of nitrous acid. At the end of the operation the Geissler's bulbs were quickly detached, and the acid blown out by a rapid stream of carbonic acid. While the experiment was proceeding the bulbs were kept in a water-bath, the temperature of which was carefully regulated; the passage of the nitric oxide was kept as uniform as possible.

The following table contains the results of the first set of experiments; not only of the actual amounts of nitric acid, and of nitrous acid, *i.e.*, the reducing power, are given, but also of the percentage amounts of these acids, taking the total acidity as 100:—

Series I.

Temperature, 22·5°.

	Time.	Nitric acid in 1 c.c.	Nitrous acid in 1 c.c.	Percentage rates.
	hours.	gram.	gram.	
—	—	0·2549	nil	100 : 0
After passage of nitric oxide	4	0·2404	0·0168	93·47 : 6·53
" " "	8	0·2409	0·0164	93·62 : 6·38

These results show that the phenomenon, whether of reaction or of solution, was complete at the end of the first interval of time; but, taken by themselves, they would not suffice to distinguish under which category the change is to be classified. Accordingly a series of experiments were conducted in which the only variable condition was that of temperature, for, as pointed out above, if the nitric oxide

is merely dissolved, then the reducing power would diminish with increase of temperature, but if a chemical change takes place, then its amount would depend upon the relative intensities of the chemical change represented by the equations given.

Series II.

Temperature, 9°.

	Time.	Nitrous acid in 1 c.c.	Nitrous acid in 1 c.c.	Percentage rates.
—	hours.	gram.	gram.	
After passage of nitric oxide	—	0·2549	nil	100 : 0
	3	0·2496	0·0169	93·66 : 6·34

Series III.

Temperature, 27·5°.

	hours.	gram.	gram.	
—	—	0·2549	nil	100 : 0
After passage of nitric oxide	4	0·2336	0·0171	93·18 : 6·82
" " "	8	0·2362	0·0169	93·69 : 6·31

Series IV.

Temperature, 32°.

	hours.	gram.	gram.	
—	—	0·2549	nil	100 : 0
After passage of nitric oxide	3	0·2318	0·0223	91·22 : 8·76

Series V.

Temperature, 42°.

	hours.	gram.	gram.	
—	—	0·2549	nil	
After passage of nitric oxide	3	0·2372	0·016	93·68 : 6·32

Series VI.

Temperature, 52°.

	hours.	gram.	gram.	
—	—	0·2549	nil	
After passage of nitric oxide	3	0·2366	0·0136	94·56 : 5·44

It will be evident from the above experiments that the ratio of nitrous to nitric acid increases slightly with rise of temperature up to 32°, but from this point it decreases so that the values at 9° and 42° are nearly identical.

These results, in the case of acid of the concentration used, would seem to indicate that the phenomenon is not entirely one of solution, but partly also of reversible chemical changes, the difference in their relative intensities being greatest at or about 32°, and least at 52°, a temperature at which nitrous acid by itself would be very rapidly decomposed. These results were also confirmed by experiments conducted with a sample of acid of half the concentration of that used above.

Concentration of nitric acid = 0.1279 gram.

Series VII.

Temperature, 22°.5.

Time.	Nitric acid in 1 c.c.	Nitrous acid in 1 c.c.	Percentage ratio.
hours.	gram.	gram.	
3	0.1257	0.0124	89.79 : 10.21
4	0.1276	0.0136	90.37 : 9.63

Series VIII.

Temperature, 32°.

hours.	gram.	gram.	
3½	0.1203	0.0137	89.78 : 10.22

Series IX.

Temperature, 42°.

hours.	gram.	gram.	
3	0.1185	0.0114	91.22 : 8.78

Series X.

Temperature, 52°.

hours.	gram.	gram.	
3	0.1274	0.0088	93.54 : 6.46

In these sets of experiments, also, the amount of nitrous acid formed increases up to a temperature of 32° , and from this point again decreases. Further from comparison of results obtained with the two samples of acid at the same temperature it is evident the percentage ratio of nitrous acid is *increased with decrease of concentration*. To confirm this a further series of experiments were conducted with an acid of one-fourth of the concentration of that used in the first set.

Concentration of acid = 0.0655 gram in 1 c.c.

Series XI.

Temperature, $22^{\circ}\cdot5$.

Time.	Nitric acid in 1 c.c.	Nitrous acid in 1 c.c.	Percentage ratio.
hours.	gram.	gram.	
$4\frac{1}{2}$	0.0662	0.0097	87.22 : 12.78
2	0.0661	0.0088	88.25 : 11.75

Series XII.

Temperature, 32° .

hours.	gram.	gram.	
3	0.0624	0.0097	86.55 : 13.45
2	0.0634	0.0105	85.79 : 14.21

Series XIII.

Temperature, 42° .

hours.	gram.	gram.	
3	0.0630	0.0081	88.61 : 11.39

Series XIV.

Temperature, 52° .

hours.	gram.	gram.	
3	0.0652	0.0062	91.31 : 8.69

The results given in the four tables above are perfectly in accordance with those of the preceding series, the maximum value for the

amount of nitrous acid being as before at a temperature of 32° ; they also show that with decrease of concentration the percentage ratio of nitrous acid is increased, though its total amount is decreased. Experiments were then conducted with acids of greater concentration, the results of which are given below.

Concentration of acid = 0.3457 gram in 1 c.c.

Series XVI.

Temperature, 22° .

Time.	Nitric acid in 1 c.c.	Nitrous acid in 1 c.c.	Percentage ratio.
hours. 3	gram. 0.3254	gram. 0.0268	92.39 : 7.61

Series XVII.

Temperature, 32° .

hours. 3	gram. 0.3253	gram. 0.0212	93.88 : 6.12
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Series XVIII.

Temperature, 42° .

hours. 3	gram. 0.3080	gram. 0.0173	94.68 : 5.32
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Concentration of acid = 0.6338 gram in 1 c.c.

Series XIX.

Temperature, $22^{\circ}.5$.

Time.	Nitric acid in 1 c.c.	Nitrous acid in 1 c.c.	Percentage ratio.
hours. 3	gram. 0.5940	gram. 0.0397	93.74 : 6.26
3 (expt. re- peated).	0.5791	0.0408	93.42 : 6.58

Series XX.

Temperature, 32°.

hours. 3½	gram. 0·5306	gram. 0·0295	94·74 : 5·26
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The liquids obtained in the experiments detailed above were of a *blue* tint, but it was also observed that in the case of the more concentrated acids red fumes were evolved to a slight extent, thus showing under these conditions a more complex reaction than the simple reversible change given above. It is also to be noticed that the sum of the quantities of nitrous and nitric acids found are less than the quantity of nitric acid originally taken, thus showing that some unaccounted-for destruction of the acid had taken place. In a set of experiments with more concentrated acids the evolution of fumes and the destruction of the acid were further noticeable.

Concentration of acid = 1·089 gram in 1 c.c.

Series XXI.

Temperature, 22°·3.

Time.	Nitric acid in 1 c.c.	Nitrous acid in 1 c.c.	Percentage ratio.
hours. 1½	gram. 0·8704	gram. 0·0632	93·25 : 6·75
2 (expt. repeated)	0·8700	0·0664	92·91 : 7·09

Series XXII.

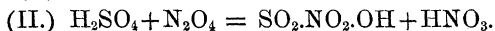
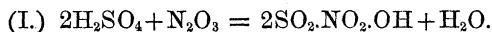
Temperature, 27°.

hours. 1½	gram. 0·7009	gram. 0·0391	94·72 : 5·29
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In the above series of experiments, when the nitric oxide gas was first passed in a yellow colour was produced, but this speedily changed into a deep *green* tint. It thus appeared that nitrogen peroxide was at first produced and this was converted, possibly by the nitric oxide and possibly, also, by the water present, into the green acid which certain writers have considered to have the composition $N_2O_3 \cdot N_2O_3 \cdot H_2O$;

such an acid, however, would contain nearly 50 per cent. of nitrous acid.

After most of the experimental work above detailed had been performed, a paper appeared by F. Marchlewski,* entitled "Zur Kenntniss der verschiedenen Färbungen der Salpetersäure," in which the author describes various experiments upon the reaction between nitric oxide and nitric acid. The main object of the paper was to determine the composition of the various coloured liquids produced when nitric oxide, nitrous fumes, and nitrogen peroxide are passed into nitric acid of different concentration. The method employed consisted in preparing such liquids and then decolorising them by a current of carbonic anhydride; the gases evolved were passed into sulphuric acid and the solution subjected to analysis. The process is based upon the observations of Lunge that nitrous fumes give under these conditions nitrosyl sulphuric acid, while nitrogen peroxide gives a mixture of nitrosyl sulphuric and nitric acids, thus :—



It might appear open to question whether the composition of these liquids can be ascertained by this indirect method, and whether a liquid apparently decolorised contains nothing but the residual nitric acid (more or less diluted) of the operation. My own experience has shown that it is extremely difficult to remove the last traces of the yellow colour from the more concentrated acids; though, on the other hand, it must be allowed that the method of analysis adopted in the text would not distinguish between nitrous acid on the one hand and nitrogen peroxide on the other, the latter of which would appear in the course of analysis as an equimolecular mixture of nitrous and nitric acids. These remarks would, however, apply probably only to the two last series of experiments. Marchlewski gives no observations of time, temperature, or degree of humidity of gases, whether oxides of nitrogen or carbonic anhydride, nor a single control analysis of the residual nitric acid. Some proof is given that the difference between the *green* and *blue* acids is dependent upon not only the water present but also upon the dissolved nitric oxide. Marchlewski seems to be quite unaware of the observations of Pélégot,† made nearly forty years ago, upon the same subject.

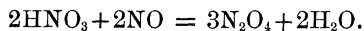
* 'Ber. Deut. Chem. Ges.,' vol. 24, p. 3271.

† 'Ann. Chim. Phys.' [III], vol. 2, p. 58. The remarks of Pélégot seem worth transcribing, as having possibly fallen into undeserved oblivion: "Comme l'acide azoteux pur paraît être bleu tandis que l'acide azotique et l'acide hypoazotique mélangés sont jaunes, on obtint par cette action de l'eau" (viz., upon nitrogen peroxides) "selon les proportions employées les différents nuances de vert et de bleu

Certain experiments were made upon the action of dry nitric oxide upon nearly anhydrous nitric acid (sp. gr. $7/7^{\circ} = 1.5326$), the preparation of which has been described in a previous section. The air was driven out of the apparatus by a current of carbonic acid dried by passage through a wash-bottle containing concentrated sulphuric acid, and then through three drying tubes filled with pumice and phosphorus pentoxide. The nitric acid was contained in the Geissler's bulbs as before (kept at a temperature of 11°), and subsequent to them was another wash-bottle of sulphuric acid to prevent the access of moisture by backward diffusion.

On passage of the nitric oxide gas, the portion of acid in the first bulb was turned a yellow tint, which gradually deepened to an orange-red; when about a litre of the gas had been driven through a red oil appeared floating upon the surface of the acid, and a few minutes after the red oil turned a green tint, and for some time there were two distinct liquids of different densities in the bulb, but afterwards a green uniform liquid was obtained. Meanwhile the portion of acid in the second bulb had deepened in tint, then the red oil was formed, and the other phenomena in due succession. (The weight of the acid at this point had increased.) When about 4 litres of nitric oxide had passed in the green liquid in the first bulb gradually turned to a blue, which slowly evaporated into the second bulb, and eventually only a few drops of an almost colourless liquid were left. Simultaneously the portion of acid in the third bulb showed the transition tints of yellow to orange with ultimate formation of the red oil, and also dense red fumes passed out of the acid. At this point the experiment was stopped, and the weight of the nitric acid was found to have considerably decreased.

The explanation of these changes, which were observed in part by Priestley* at the end of the last century, seems to be as follows:—At first nitrogen peroxide is formed by the mutual oxidation of the nitric oxide and reduction of the nitric acid, and this is retained in solution by the excess of the acid



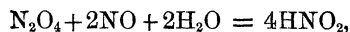
A point is reached at which the acid becomes supersaturated, and the

. . . qui se développent également par l'action du bioxyde d'azote sur l'acide azotique à différents degrés de densité.

"Le produit vert . . . se forme aussi par le contact du bioxyde d'azote avec l'acide hypoazotique, et sa production pouvait être tout à fait indépendante de l'eau" (as shown by experiment).

* "Experiments and Observations on different kinds of Air," vol. 1, p. 383. I may be allowed to allude to the section of this work relating to nitrous acid, which contains a number of observations upon its properties; several of them appear to have been published as novelties many years afterwards.

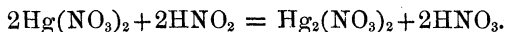
excess of the peroxide separates out (the red oil). According to the experiments of Péligré, nitric oxide passed into this gives a green liquid. The absorption and retention of the nitrogen peroxide accounts for the gain in weight (about one-sixth) of the acid. The reduction then proceeds further, and nitrous acid (the blue liquid) is produced, thus:—



and this is evaporated by the continued current of the nitric oxide, leaving finally only the water originally present, both free and combined, in the nitric acid. This destruction of the nitric acid accounts for the loss in weight. As Priestley wrote: "Towards the end of the process (of absorption of nitrous air by pale-yellow spirit of nitre), the evaporation of the acid was perceived to be very great, and when I took it out the quantity was found to be diminished by one-half. Also, it had become, by means of the process and evaporation together, exceedingly weak, and was rather blue than green."

Reaction between Nitric Oxide and Mercuric Nitrate in Nitric Acid Solution.

In my former paper* it was shown that when a current of hydrogen was passed through a solution of mercuric nitrate in nitric acid solution, the mercuric was reduced to a mercurous salt without any considerable formation of nitrous acid, which was, however, produced in abundance when cupric nitrate was subjected to the same action. As it seemed probable that the nitrous acid which might have been produced in the former operation was in reality used up in the reduction of the mercuric salt, the experiment was repeated in precisely similar manner, nitric oxide being substituted for hydrogen. It was found, as before, that the mercuric salt was reduced; from 0.5 gram mercuric oxide dissolved in nitric acid (1 c.c. containing 0.2549 gram acid) after passage of nitric oxide for $3\frac{1}{2}$ hours at a temperature of 35° , 0.019 gram of mercurous chloride was obtained, while from a similar portion, through which the nitric oxide had not been passed, 0.0018 gram was precipitated. It is probable, then, that the hydrogen in the former experiments reduced at first the free nitric into nitrous acid, which in its turn reduced the mercuric nitrate, thus:—



No free nitrous acid would therefore appear in the course of the operation.

* 'Phil. Trans.,' 1891, A, p. 315.

Summary of Results.

I. The reaction between nitric oxide and nitric acid varies with the concentration of the acid and the temperature; with more concentrated acids nitrogen peroxide is at first formed and then nitrous acid; with less concentrated acids the latter is produced at once.

II. Only with quite dilute acids (of 30 per cent. concentration and below) does the reaction between the nitric oxide and nitric acid appear to be reversible; the average value for $p/q = 9$ (p = quantity of nitric, q of nitrous, acid), though the actual value varies from 3 to 4 per cent. on either side, according to the conditions of the experiment.

III. With more dilute acids the amount of nitrous acid formed at first increases slightly and then decreases with the temperature; but with more concentrated acids the amount uniformly decreases.

IV. The proportional quantity of nitrous acid formed increases with decrease of concentration, but the actual quantity is of course less.

It would appear that the simple reversible reaction between nitric oxide and nitric acid becomes modified with acids above a concentration of about 30 per cent. and a temperature of 32° . These were also approximately the limits of concentration and temperature, above which the reactions between metals and nitric acid could not be prevented by substances such as urea, potassium chlorate, and the like. I will, however, merely allude to the point without wishing to lay an undue stress upon possibly nothing but chance coincidences.

The Rate of Decomposition of Nitrous Acid.

The velocity of the decomposition of nitrous acid, presumably in nitric acid solution, has been made the subject of a previous investigation by Clemente Montemartini (*vide supra*). As a result of several series of experiments this writer considers that the rate of this decomposition may be expressed by the differential equation

$$(I.) \frac{dC}{dT} = kC \quad \text{or} \quad (II.) k = \frac{1}{T} \log \frac{C_0}{C_1},$$

in which C is the concentration, T the time, and k is a constant.

This equation will be discussed in the sequel. My experiments were commenced primarily with a view of ascertaining if nitrous acid is the more stable the greater the proportion of nitric acid present, a point which was raised in the course of my investigations on the reactions of nitric acid and metals. Further, it seemed probable that the presence of metallic salts might also affect the stability of nitrous acid, as Armstrong and Acworth* allude to the persistence with

* 'Chem. Soc. Journ.,' 1877 (II), p. 54.

which the nitrous acid is retained by solutions containing the products of the reaction between nitric acid and metals. It also seemed possible that such a line of inquiry might throw some light upon the nature of an acid intermediate between nitrous and nitric acids, in whose existence certain writers believe, though the facts adduced at present are perhaps hardly sufficient to warrant such a belief.

The apparatus and method of experiment finally adopted were as follows:—The nitrous acid solution was placed in a cylindrical tube containing 100 c.c. up to a certain mark; at its upper end were two apertures, into one of which was sealed a glass delivery tube, while the other could be wholly or partially closed by a small rubber plug through which passed a pipette of exactly 2 c.c. capacity. The former, which served for the passage of a stream of carbonic acid, was sealed off at its lower end, the gas passing through a small pin-hole at the side, and thus not directly impinging upon the liquid; the space between the loosely-fitting plug and the glass wall serving for its exit. At the end of certain intervals of time the plug was rammed in, whereby the pressure of the gas forced the liquid up the pipette; when this was filled up to the graduation mark the sample was removed for analysis, while the aperture of the cylindrical tube was partly closed meanwhile by a duplicate plug. The cylinder was immersed in a water-bath, the temperature of which was kept constant to within one-tenth of a degree on either side of that required. Before any observations were made the ratio of nitrous to nitric acid present was determined.

Nitrous Acid from Silver Nitrite and Hydrochloric Acid.

The solution of nitrous acid was prepared in the usual manner by the decomposition of recrystallised silver nitrite with a slight deficiency of hydrochloric acid, and the liquid filtered from the precipitated silver chloride into the decomposition flask. The amount of nitrous acid was determined at the end of fixed intervals of time, generally half an hour, and the results calculated on the hypothesis that the volume of the liquid was maintained constant throughout the course of the experiment.

In the following table the results obtained are set forth, in which T is the time from start, and C the concentration of the solution.

Series XXIII.

Volume of solution = 60 c.c. Temperature, $24^{\circ}9 \pm 0.1$.

Ratio of nitrous to nitric acid = 1 : 3.86.

T.	C.	T.	C.
'	gram.	'	gram.
0	0.3063	120	0.2306
30	0.2793	150	0.2130
60	0.2559	180	0.2017
90	0.2413	210	0.1890

These results are expressible by the formula

$$\log (T+t) + \log C = \log k,$$

in which T is the time from start, and t an interval of time which would have elapsed from the moment at which, conditions remaining otherwise the same, the amount of nitrous acid was infinitely great, namely, $C = \infty$, and that moment at which the experiment was actually commenced, C is the concentration, and k is a constant.

In the above series the value for t is taken as 320', and in the table below are given the values for $\log (T+t)$, $\log c$, and $\log k$.

$\log (T+t)$.	$\log C$.	$\log k$.
2.5051	1.4861	1.9912
2.5441	1.4461	1.9902
2.5798	1.4080	1.9878
2.6128	1.3825	1.9953
2.6335	1.3629	1.9964
2.6627	1.3283	1.9910
2.6901	1.3046	1.9947
2.7160	1.2764	1.9924

The values in the third column show great concordance; if the mean 1.992 be taken and the results calculated therefrom, the observed and calculated values for the concentration of the nitrous acid will compare as follows:—

C (observed).	C (calculated).	C (observed).	C (calculated).
gram.	gram.	gram.	gram.
0.3063	0.3071	0.2306	0.2285
0.2793	0.2808	0.2130	0.2138
0.2539	0.2586	0.2017	0.2006
0.2413	0.2397	0.1890	0.1890

The greatest difference occurs in the third value, which is rather less than 2 per cent., which can readily be accounted for by errors of experiment in dealing with a substance so susceptible of decomposition as nitrous acid. The curve which represents the concentration of the acid in terms of time is a portion of a hyperbola, the differential equation of which is

$$\frac{dC}{dT} = -\frac{C^2}{M},$$

which expresses the rate at which equivalent masses react, whether it be of the nitric with the nitrous acid, or the nitrous acid with itself; in each experiment $1/M$ is the amount of each unit mass which reacts with the other per unit time when an unit mass of each substance is present.

If Clemente Montemartini's equation $dc/dT = kC$ is correct, there should be two reacting substances, one of constant concentration throughout the reaction. It is, however, to be observed that the values given for the constant k in his results differ widely among themselves, often as much as 25 per cent. between the maximum and minimum. Further, all the results in each set of experiments are referred to the first, the C_0 of equation (ii), though there is no especial reason that this analytical determination should be more exact than those subsequent to it. With the general purport, however, of Montemartini's paper I cannot but completely agree, namely, that the rate of decomposition of nitrous acid is dependent upon the tension of the superincumbent nitric oxide, without, however, necessarily committing oneself to the view that herein is presented a "true case of dissociation."

It is worthy of remark that the curve representing the decomposition of nitrous acid is exactly identical with that of a previous case of chemical change investigated by myself, namely, the decomposition of formic acid into carbonic oxide and water,* in which the method of observation was precisely the reverse of that adopted in this research. For, herein, the concentration is determined at equal intervals of time, but in the previous case observations were made of the times required for equal diminution of concentration. The results of other series of experiments are given below, the observed and calculated values for the concentration of the nitrous acid being compared in each instance.

* 'Phil. Trans.,' 1888, A, p. 290.

Series XXIV.

Volume of solution = 70 c.c. Temperature, 25°·5.

Ratio of nitrous to nitric acid = 1 : 2·13.

T.	C (observed).	C (calculated). $t = 400$. $\log k = 1\cdot250$.
'	gram.	gram.
0	0·4382	0·4448
30	0·4009	0·4147
60	0·3915	0·3877
90	0·3673	0·3640
120	0·3460	0·3430
150	0·3231	0·3244
180	0·2979	0·3075
210	0·2966	9·2924
240	0·2836	0·2851
270	0·2714	0·2661

Series XXV.

Volume of solution = 60 c.c. Temperature, 25°·0.

T.	C (observed).	C (calculated). $t = 170$. $\log k = 0\cdot856$.
'	gram.	gram.
0	0·4157	0·4237
30	0·3646	0·3606
60	0·3190	0·3134
90	0·2881	0·2774
120	0·2484	0·2489
150	0·2381	0·2250
180	0·2102	0·2209
210	0·1894	0·1901
240	0·1647	0·1679

Series XXVI.

Volume of solution = 70 c.c. Temperature, 24°·6 \pm 0·1.

Ratio of nitrous to nitric acid = 1 : 20·7.

T.	C (observed).	C (calculated). $t = 480$. $\log k = 1\cdot452$.
'	gram.	gram.
0	0·6707	0·6742
30	0·6262	0·6270
60	0·5789	0·5899
90	0·5537	0·5547
120	0·5255	0·5255
150	0·5065	0·4968
180	0·4775	0·4719

In all the above series of experiments the observed and calculated results are as nearly approximate as can be expected, considering the great instability of the nitrous acid, which is appreciably decomposing even in the brief interval of time required for the transference of the solution from the decomposition flask into the potassium permanganate. In the last series of experiments quoted above, in which a considerable proportion of nitric acid was purposely introduced, it is to be noticed that the rate of decomposition is decreased, even though the mass of nitrous acid originally present was greater, which should of course produce an exactly opposite result. This would, therefore, seem to indicate that nitrous acid is more stable in the presence of excess of nitric acid.

Nitrous Acid from Nitric Oxide and Nitric Acid.

Nitric oxide gas was passed into concentrated nitric acid until a deep green liquid was obtained; 10 c.c. of this were then slowly introduced into about five times its bulk of water, and the whole volume finally made up to 100 c.c.

Series XXVII.

Volume of solution = 100 c.c. Temperature, $27^{\circ}7 \pm 0.1$.

Ratio of nitrous to nitric acid = 1 : 10.1.

T.	C (observed).	C (calculated). $t = 360$.
/	gram.	gram.
0	0.8812	0.8910
30	0.8372	0.8227
60	0.7749	0.7637
90	0.7021	0.6967
120	0.6791	0.6684
150	0.6443	0.6290
180	0.5874	0.5805
210	0.5603	0.5627
240	0.5242	0.5347
270	0.4965	0.5093

The curve representing the course of decomposition of the nitrous acid obtained by this method is precisely identical with that of the nitrous acid from the silver nitrite; though the rate of decomposition is somewhat diminished. For if the series above be compared with Series XXV, which lasted for the same duration of time, yet though the mass undergoing change was nearly twice as great, and the temperature 2° higher, both of which conditions would increase the rate, yet there is a difference of only 5 per cent. in the amount of nitrous

acid which has disappeared in the two cases. This result confirms that of the immediately preceding series in showing the increase of the stability of nitrous acid in the presence of nitric acid.

Another set of experiments was conducted, the condition of temperature being varied.

Series XXVIII.

Volume of solution = 100 c.c. Temperature, $11^{\circ}1$ to $11^{\circ}3$.

Ratio of nitrous to nitric acid = 1 : 10.72.

T.	C (observed).	C (calculated). $t = 860$. $\log k = 1.8811$.
	gram.	gram.
0	0.8910	0.8823
30	0.8716	0.8545
60	0.8467	0.8266
90	0.8046	0.8006
120	0.7815	0.7761
150	0.7595	0.7531
180	0.7337	0.7314
210	0.7033	0.7108
240	0.6759	0.6914
270	0.6710	0.6739
300	0.6454	0.6537

A third set of experiments was also conducted at a higher temperature, other conditions remaining the same.

Series XXIX.

Volume of solution = 100 c.c. Temperature, $31^{\circ}2$.

Ratio of nitrous to nitric acid = 1 : 10.13.

T.	C (observed).	C (calculated). $t = 330$. $\log k = 1.3268$.
	gram.	gram.
0	0.6565	0.6432
30	0.6030	0.5893
60	0.5542	0.5443
90	0.4939	0.4712
150	0.4451	0.4422
180	0.4169	0.4162
210	0.3970	0.3930
240	0.3545	0.3720
270	0.3344	0.3538

On a comparison of the results set forth in the three preceding series of experiments, it appears that the velocity of decomposition of nitrous acid is an exponential function of the temperature, the former

increasing in geometrical as the latter increases in arithmetical proportion. This relation may be expressed by the equation

$$v_t = vk^{(t-t_1)},$$

that is to say, the difference of the logarithms of the amounts of nitrous acid decomposed at the end of a given interval of time will be constant for a constant difference of temperature. This is rendered evident by the following comparison:—

Series.	Temp.	Percentage loss after 270°.	Logarithms.
(I)	11·2°	24·00	1·3802
(II)	27·7	43·01	1·6334
(III)	31·2	49·09	1·6909

The logarithmic differences for 1° are therefore:—

From (I) and (III)	0·0153
„ (I) „ (II)	0·0154
„ (II) „ (III)	0·0167
Mean.....	0·0158

The rate of chemical decomposition of the nitrous acid is therefore practically doubled for every 20°, which would give a constant logarithmic difference of 0·0151 for every degree. In this respect this change resembles another, otherwise totally different from it, namely, that between marble and hydrochloric acid,* which varies by a like amount for equal differences of temperature. This relation is also exemplified by another pair of experiments in which 20 c.c. of nitric acid through which nitric oxide gas had been passed were made with water up to a constant volume of 100 c.c.

Series XXX.

Volume of solution = 100 c.c. Temperature, 21°·8.

Ratio of nitrous to nitric acid = 1 : 10·2.

T.	C (observed).	C (calculated). $t = 400$. Const. log. = 1·7307.
	grams.	grams.
0	1·3247	1·3451
30	1·2522	1·2512
60	1·1188	1·1175
90	1·0948	1·0978
150	0·9992	0·9781
180	0·9111	0·9275
210	0·8688	0·8799
240	0·8254	0·8405
270	0·7895	0·8010

* Spring, 'Zeit. Physikal. Chem.,' vol. 1, p. 219.

Series XXXI.

Volume of solution = 100 c.c. Temperature, 31°1.

Ratio of nitrous to nitric acid = 1 : 10·34.

T.	C (observed).	T.	C (observed).
'	grams.	'	gram.
0	1·4432	190	0·8219
30	1·2868	220	0·7441
60	1·2045	250	0·6495
90	1·0720	270	0·6045
120	0·9679	300	0·5509

Percentage loss after 270'

in series 58·05 Logarithm 1·76385

Do. do. .. 40·40 „ 1·60655

Logarithmic difference } 0·0168
for 1°

This difference is practically identical with those given above, though the masses of nitric and nitrous acids present were twice as great in the latter as in the former series of experiments.

Nitrous Acid from Nitrogen Peroxide and Water.

About 1—2 c.c. of nitrogen peroxide were slowly added to 50 c.c. of water, the liquid being kept continually stirred; after the mixture had become uniform the volume was made up to 100 c.c. as before. By this means a dilute solution of nitrous and nitric acids was obtained. The method of experiment was conducted as usual.

Series XXXII.

Temperature, 21°8.

Nitrous acid present after complete admixture = 1·0663 grams.

Nitric acid „ „ = 2·3544 grams.

Ratio of nitrous to nitric acid = 1 : 2·12.

T.	C (observed).	C (calculated). $t = 1030$. Const. log = 1·9819.
'	gram.	gram.
0	0·9181	0·9292
30	0·9151	0·9049
60	0·8952	0·8801
90	0·8597	0·8560
120	0·8373	0·8341
150	0·8171	0·8129
180	0·7819	0·7927
210	0·7618	0·7718
240	0·7538	0·7553
270	0·7381	0·7389

The table below contains the results of another set of experiments with a more dilute solution.

Series XXXIII.

Temperature, 21°·8. Nitrous acid = 0·7292 gram. Nitric acid = 1·5457 grams. Ratio = 1 : 2·02.

T.	C (observed).	C (calculated). $t = 500$. Const. log. = 1·5587.
'	gram.	gram.
0	0·7292	0·7247
30	0·6811	0·6830
60	0·6401	0·6464
90	0·6166	0·6279
120	0·5843	0·5840
150	0·5570	0·5543
210	0·5095	0·5080
240	0·4856	0·4892
270	0·4736	0·4702
300	0·4502	0·4525

Series XXXIV.

Temperature, 31°·8. Nitrous acid = 2·4557. Nitric acid = 2·2571.
Ratio of nitrous to nitric acid = 1 : 0·93.

T.	C (observed).	C (calculated). $t = 160$. Const. log = 1·5692.
'	grams.	grams.
0	2·2321	2·3180
30	1·9764	1·9077
60	1·6981	1·6858
90	1·4778	1·4833
165	1·1924	1·1413
180	1·1081	1·0937
210	0·9986	1·0024
240	0·9010	0·9271

The greatest difference between the observed and calculated results is shown in the first two experiments, but this can in part be accounted for by the difficulty experienced in introducing the nitrous acid solution into the permanganate before that some of the liquid was projected from the measuring vessel by the rapidly evolved nitric oxide gas. The above three series of experiments show that whether the nitrous acid, produced from nitrogen peroxide and water, is of a concentration of 0·45 per cent., or five times that amount, the rate of

decomposition is in accordance with the mathematical formulæ given, since, as it happened by chance, the Series XXXII to XXXIV were continuous as regards the masses of nitrous acid contained therein.

Nitrous Acid from Nitrous Fumes and Water.

When nitrous fumes, from arsenious oxide and nitric acid, are passed into water at ordinary temperatures of 12—15°, their absorption is apparently very incomplete; a liquid is obtained nearly colourless, and containing 1 to 2 per cent. of free nitrous acid. This solution gives off bubbles of gas very freely, especially when poured from one vessel to another, thus calling to mind the behaviour of solutions of hydrogen peroxide. This very rapid evolution of gas introduced, as explained above, unavoidable errors in the method of experiment adopted; there is therefore not so complete an accordance between the observed and calculated values as in the other series of experiments.

Series XXXV.

Temperature, 31°·7. Nitrous acid = 0·7685 gram. Nitric acid = 0·6753 gram. Ratio of nitrous to nitric acid = 1 : 0·88.

T.	C (observed).	C (calculated). $t = 160$. Const. log = 1·0927.
/	gram.	gram.
0	0·7685	0·7697
60	0·5665	0·5628
90	0·4828	0·4953
170	0·3898	0·3752
200	0·3501	0·3439
230	0·3342	0·3174
260	0·2963	0·2948

The rate of decomposition is nearly identical with that of Series XXXIV, conducted at the same temperature, and in which the ratio of nitrous to nitric acid was also nearly identical.

Series XXXVI.

Temperature, 19°·8. Nitrous acid = 1·1789 grams. Nitric acid = 0·3973 gram. Ratio of nitrous to nitric acid = 1 : 0·34.

T.	C (observed).	C (calculated). $t = 160$. Const. log = 1·2561.
/	grams.	grams.
0	1·1789	1·200
30	0·9680	1·0008
60	0·8453	0·8589
90	0·7853	0·7513
120	0·7109	0·6674
180	0·5444	0·5440
210	0·5022	0·5022
240	0·4703	0·4624
270	0·4317	0·4294
300	0·4068	0·4008

It follows, therefore, from the experiments the details of which are given above, that solutions containing both nitrous and nitric acids, whether prepared from silver nitrite and hydrochloric acid, or from nitric oxide and nitric acid, or from nitrogen peroxide and water, or from nitrous fumes and water, have this one property in common, that the diminution of reducing material, presumably nitrous acid, therein contained, proceeds in accordance with the same law. The velocity of the change seems, however, to be dependent rather upon the ratio of nitrous to nitric acid than upon the actual masses of either of them. But though these solutions have this one point in common, yet in other respects they differ most markedly. For bubbles of gas, namely nitric oxide, are rapidly given off from solutions prepared from nitrogen peroxide and nitrous fumes, and to a less degree from silver nitrite, though solutions from nitric oxide and nitric acid do not give off bubbles of gas in a similar manner. Again, all my former investigations* have shown that, whereas metallic lead does not readily dissolve in solutions containing nitrous acid, and prepared from silver nitrite, yet it dissolves very rapidly in solutions equally containing nitrous acid, but prepared from nitrogen peroxide and water. The cause for the similarity on the one hand, and the dissimilarity on the other, must remain the subject of a fuller enquiry.

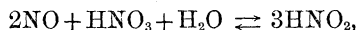
General Conclusions.

The main points of this enquiry may briefly be summarised as follows:—

* 'Soc. Chem. Industry JI.,' 1891, p. 1294.

(i.) The formation of the impurity of nitrogen peroxide in nitric acid, imparting to it the well-known yellow tint, takes place in the case of the more concentrated acid, even at a temperature of 30° , and of the less concentrated acids at from 100 — 150° , even when the acid is not unduly exposed to sunlight.

(ii.) The reaction between nitric oxide and nitric acid may be regarded as reversible, thus :—



provided that the acid be sufficiently dilute, and the temperature sufficiently low. Under these conditions equilibrium is established between the masses of nitric acids when the ratio of the former to the latter is, roughly speaking, as $9:1$. The actual ratio varies slightly on the one side or the other, according to the conditions of the experiments. With more concentrated acids and at higher temperatures the chemical changes taking place are more complicated, and the decomposition of the acid more profound.

(iii.) The decomposition of solutions containing both nitric and nitrous acids is also investigated; the rate of the change is shown to be proportional to the mass of the nitrous acid undergoing change. The curve representing the amount of chemical decomposition in terms of the mass present is shown to be hyperbolic, and illustrative of the law

$$(I.) \quad \frac{dC}{dT} = -\frac{C^2}{M}.$$

This holds good, whatever be the method employed for the production of the nitrous-nitric acid solution.

The observed values for C or the concentration of the nitrous acid are concordant with those calculated according to the above differential equation within the limits of experimental error.

The rate is dependent upon the ratio of the masses of the nitrous and nitric acid, being the more rapid, the greater the proportion of the former to that of the latter.

In the particular case of the liquid prepared from nitric oxide and nitric acid, wherein the reproduction of solutions of similar concentration presents less difficulty, it is shown that as the temperature increases in arithmetical the rate of change increases in geometrical proportion, in accordance with the equation

$$(II.) \quad v_t = v, k^{(t-t_1)},$$

the value for k being 0.0158 .

Finally, though the nitrous-nitric acid solutions behave in a similar manner as regards the diminution of the mass of the nitrous acid, yet, in other respects, such as evolution of gases and the action upon metals, they are dissimilar.

In conclusion, I would express my obligations to Mr. W. Esson for assistance in the mathematical portion of the paper, and to my colleagues for suggestions made in the course of the investigations.

VII. "On the Theory of Electrodynamics, as affected by the Nature of the Mechanical Stresses in Excited Dielectrics."

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1. A theory of electrodynamics was first precisely developed by Maxwell, which based the phenomena on Faraday's view of the play of elasticity in a medium, instead of the conception of action at a distance, by means of which the mathematical laws had been primarily evolved. The electromotive equations of Maxwell however involve nothing directly of the elastic structure of this medium, which remains wholly in the background. They involve simply the assumption of a displacement across dielectrics with such properties as to make all electric currents circuital; all the equations of Ampère and Neumann for closed or circuital currents have then a universal validity, and no further hypothesis is required for the full development of the subject.

The theory was next discussed by Helmholtz in his memoirs on electrodynamics, in a way which took direct advantage of the picture of a polarised dielectric supplied by Mossotti's adaptation of the Poisson theory of induced magnetisation. Stated absolutely, this simply builds upon the assumption that at each point in the excited dielectric there is something which has the properties of a current element (electric transfer or displacement), which is represented both in direction and magnitude by the electric force at the point multiplied by a constant factor; no more general starting point seems possible for an isotropic dielectric. The development of this hypothesis, exactly on the analogy of a similar discussion with the Poisson-Mossotti phraseology in a previous paper,* leads to the necessity of recognising the existence of absolute electric charges on the faces of an excited condenser; so that the exciting current causes the accumulation of these charges, and therefore is not circuital or solenoidal. This defect of circuital character however practically disappears in the limiting case when the constant ratio of the polarisation to the electric force is extremely great; and then the theory becomes a concrete illustration of the general statements of Maxwell with respect to electric displacement.